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TEMPERATURE DEPENDENCE OF THE FLUORESCENCE LIFETIME OF BENZENE

IN CRYOGENIC SOLUTIONS

by

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Fluorescence lifetimes for C_6D_6 in various hydrocarbon solvents have been measured as a function of concentration and temperature. For the solvents ethylene, ethane, and propane it is found that at low concentrations (~ 0.3 ppm or $\sim 4 \times 10^{-6}$ mole/ℓ) the fluorescence lifetime is roughly temperature independent ($90 \leq T \leq 220K$) and equal to the gas phase value of ~ 150 ns. As the concentration is increased ($1 \leq c \leq 100$ ppm) the lifetime decreases as temperature is increased reaching a minimum value at about 150K of roughly 70-100 ns, depending on the concentration. As the temperature is increased

from 150K to 220K, the lifetime increases to well over 100 ns. These trends can be understood on the basis of a monomer/excimer kinetic model in which benzene excimers form at low temperature and break apart at high temperature to regenerate the excited state and ground state monomers. In propene and 1-butene solvents, such behavior is not observed most likely due to solvent triplet state quenching of the excited $^1B_{2u}$ benzene monomer.

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ABSTRACT

Fluorescence lifetimes for C_6D_6 in various hydrocarbon solvents have been measured as a function of concentration and temperature. For the solvents ethylene, ethane, and propane it is found that at low concentrations (~0.3 ppm or ~4 x 10^{-6} mole/ℓ) the fluorescence lifetime is roughly temperature independent ($90 \leq T \leq 220$K) and equal to the gas phase value of ~150 ns. As the concentration is increased ($1 \leq c \leq 100$ ppm) the lifetime decrease as temperature is increased reaching a minimum value at about 150K of roughly 70-100 nsec, depending on the concentration. As the temperature is increased from 150K to 220K, the lifetime increases to well over 100 ns. These trends can be understood on the basis of a monomer/excimer kinetic model in which benzene excimers form at low temperature and break apart at high temperature to regenerate the excited state and ground state monomers. In propene and 1-butene solvents, such behavior is not observed most likely due to solvent triplet state quenching of the excited $^1B_{2u}$ benzene monomer.

I.   INTRODUCTION

The study of molecular electronic spectra of solute molecules in cryogenic molecular liquids has begun to draw increasing attention in recent years.[1] Fluorescent and phosphorescent probe molecules can provide information on local structure and microdynamics of chemical systems in liquid solution.[2] Moreover, even at low concentrations (1 ppm), or ~1.5 x 10^{-5} moles/ℓ) absorption and emission spectra are intense enough to provide good signal to noise detection ratios. Cryogenic liquids reduce the spectral congestion associated with hot bands and quite often solvent effects induce forbidden transitions by lowering the effective solute symmetry. Benzene, as a solvent probe in several cryogenic liquids, has proved helpful in studying solvent-solute interactions and liquid state structure.[3,4]

Cryogenic small molecule liquids are employed in this research because they are simple but still molecular, they are good solvents for organic molecules, they possess a wide liquid range, and their low temperature allows for sharp spectroscopic probe features.[3,4,5] Benzene is a reasonable probe system because of its high symmetry, well known spectra and kinetics, and solubility.

In the present study, fluorescence lifetimes of the first excited singlet state of benzene are reported in several cryogenic liquids. The solvents employed in these studies are methane, ethane, ethylene, propane, propene, and 1-butene. The experimental results are explained based on a monomer/dimer (excimer) kinetic model. At low temperature the "cage" structure of the liquid provides an effective mechanism for the formation of an excimer once a ground state benzene molecule has diffused to and is trapped in a cage in which there

also resides an excited state molecule. At high temperature the lifetime of this cage structure is significantly reduced by the large thermal energy available to the molecules. Dissociation of these excimers repopulates the excited state monomer and an increase in the fluorescence lifetime is observed at high temperature. It is further demonstrated that the formation of excimers is a diffusion controlled process with a high probability of excimer formation on each excited state/ground state benzene pair encounter. It is postulated that this high cross section for formation is associated with a solvent cage or coordination (solvent shell) structure. There is some evidence that $^1B_{2u}$ benzene may also relax through a high efficiency non-radiative pathway accessible at energies ~2500 cm^{-1} above the zero point energy of the $^1B_{2u}$ state; this route is only open to benzene in liquids or high pressure gases near or above room temperature, however.

II.   EXPERIMENTAL

Sample preparation and the instrumental set up have been described in other reports.[3,5] C_6D_6 (Aldrich Gold Label) and C_6H_6 (Fisher Gold Label) are further purified by vacuum distillation over potassium to remove water and other oxygen containing impurities. Solvents are all research grade of the highest obtainable commercial purity. All solvents are vacuum distilled and passed through molecular sieve, oxygen scavenger (Ridox) and activated charcoal. Samples are premixed in a 7ℓ stainless steel can. Concentrations are regulated based on the known vapor pressure of C_6H_6/C_6D_6 in calibrated volumes and fixed gas phase volume/pressure measurements for the solvent. Frequency doubled pulses from a Nd/YAG laser (Quanta-Ray DCR-1) are used to pump a rhodamine 610 dye laser. The output of the dye laser is further frequency doubled into the UV; the UV radiation is then Raman shifted in a high pressure H_2 (270 psi) cell. The first stimulated anti-Stokes line from the Raman cell is appropriate for pumping vibronic transitions of the $^1B_{2u} \leftarrow {}^1A_{1g}$ manifold in various cryogenic solvents. The energy of this unfocused beam at the sample is roughly 1-2 mJ/pulse, the pulse width is ~5 ns, and the linewidth is ~0.5 cm^{-1}. Dispersed fluorescence is detected by an RCA C31000M photomultiplier tube, the signal from which is then processed by a boxcar averager (PAR 162/164) which interfaces to a desktop computer (HP9845S). A relaxation curve is obtained as the boxcar is scanned by a ramp voltage from the computer. Typical scan times are 10 min for a 500 ns scanning range. The decay curves obtained are then fit by a single exponential decay function with an adjustable base line. The standard deviation of a number of measurements of the decay times for a given sample and temperature based on a complete fit to

the experimental decay curves is always better than 5%. Since the signals are

dispersed and the detection wave length is at the peak of a monomer transition,

only the monomer fluorescence lifetime is of concern.

III. RESULTS

Although we have data for both C_6H_6 and C_6D_6, only those results
referring to C_6D_6 will be presented and discussed in this paper. In all
respects, both molecules give essentially the same information. Decay curves
for the benzene fluorescence in liquid solutions (C_6D_6/C_2H_6) are shown in
Fig. 1. Within the stated standard deviation, as determined by computer fitting
of the entire decay curve after the first 10 ns, all decay curves could be
modeled by a single exponential function.

The resulting lifetimes of the $^1B_{2u}$ state of benzene in various solvents
as a function of temperature are shown in Figs. 2-4. For the C_6D_6/C_2H_4,
C_6D_6/C_2H_6 and C_6D_6/C_3H_8 systems, lifetime of the $^1B_{2u}$ state shows
only a small dependence on temperature at low concentrations (~0.3 ppm). This
change, over the range 90 to 220K, is roughly 10% (~150 ns to 130 ns). At low
temperatures, the fluorescence lifetimes approach the value of the low pressure
gas.[6] Temperature dependence of the lifetime becomes prominent at higher
concentrations, however. At higher temperatures with moderate concentration,
the lifetime falls to a minimum value. As the temperature further increases,
the lifetime begins to increase (see Fig. 2-4).

In order to determine the cause of this lifetime behavior with temperature
and concentration, 6×10^{-4} moles/ℓ of O_2 was added to the C_6D_6/C_2H_6
system. An overall shorter lifetime (about 20%) for the benzene emission was
observed. The same temperature dependence of lifetimes was detected, however.
Since O_2 is and effective triplet state quencher, this observation tends to
eliminate the triplet state of benzene as an effective cause of such behavior.
Both thermal depopulation of $^3B_{1u}$ to $^1B_{2u}$ and triplet-triplet annihilation

mechanisms are thus not dominant (although they may be present) in the overall
kinetic processes. Moreover, linear dependence of the fluorescent intensity on
the input laser power also seems to rule out diffusion controlled
triplet-triplet annihilition processes.

The lifetime of the $^1B_{2u}$ state in C_3H_6 and $1-C_4H_8$ was also studied
as a function of temperature and concentration. The behavior of the fluore-
scence intensity as a function of time and temperature is quite different for
these two solvents than that found for C_2H_4, C_2H_6 and C_3H_8. The lifetime
of the $^1B_{2u}$ state shows a dramatic decrease as temperature is increased; no
recovery of the low temperature lifetime is observed even at the highest
temperature (~220K). Numerous serial purifications and large variations in
benzene concentration have no effect on these results. The data are illustrated
in Fig. 5. In these two solvents self-quenching must not be the predominant
quenching mechanism.

IV. DISCUSSION

It is known that different vibronic levels of the $^1B_{2u}$ state of benzene have difference lifetimes in the gas phase at low pressures.[7] An increase in the gas pressure will result in a thermally equilibrated vibronic manifold from which one observes an average lifetime for all vibronic levels. In order to measure the lifetime of the zeroth vibrational level of the $^1B_{2u}$ state, very low pressures must be employed with excitation through a hot band transition. Such studies give a low pressure electronic lifetime of ~160 ns.[6] However, in cryogenic liquid solutions it has been demonstrated that all emission comes from the zero point state of $^1B_{2u}$ and moreover, that the observed cryogenic liquid state lifetime is about the same as the longest vibronic level lifetimes measured for the $^1B_{2u}$ state (~150 ns). Thus, it seems reasonable to assume that the electronic state lifetime of $^1B_{2u}$ is closely approximated by that lifetime observed in dilute cryogenic liquids.

The similar values of the fluorescence lifetimes of benzene in low temperature liquids and in the low pressure gas phase are consistent with the nearly identical quantum yields under these two very different sets of conditions.[8] A graphical extrapolation of the low temperature low concentration liquid lifetime to room temperature yields a lifetime of ~110 ns; this is much longer than the usually reported 20-30 ns lifetime for room temperature liquids.[9,10] The fluorescence lifetimes of the high pressure gas typically fall between these two values (20-110 ns).[6] These observations indicate that the relaxation rate from the zero point level of the excited $^1B_{2u}$ state of benzene is largely an intramolecular property not grossly perturbed by collisions. Once the excited molecule is relaxed to this level, further collisions do not readily induce direct relaxation to the lowest electronic state.

However, collisions can activate the $^1B_{2u}$ zero point molecules to higher vibrational levels in the $^1B_{2u}$ manifold; in particular, to the level at ~2500 cm^{-1} which reportedly opens a new nonradiative channel for relaxation.[8,9,11] At low temperature, thermal collisional activation to this fast relaxation pathway can be neglected; consequently, the relaxation rate is slow in low pressure gases at room temperature as the rate of activation through high energy collisions is quite slow. Thus, the conclusion is that low temperature liquid solutions of benzene and dilute gas phase benzene should have nearly the same $^1B_{2u}$ electronic state relaxation times, while room temperature benzene solutions should have much shorter relaxation times. The high frequency of collision and high thermal energy in room temperature liquids and high pressure gases effectively shortens the fluorescence lifetime of benzene through collision induced vibrational activation. The general implication of this line of reasoning is that the low temperature liquid can be construed as providing a relatively "collision free" structure (cage) for the solute. On the other hand, the high thermal energy of room temperature liquids generates high collision rates (rapidly varying or oscillating structures) with many of these collisions being of high energy, perhaps due to multiple simultaneous events.

In addition to this small temperature dependence for the fluorescence lifetime of very dilute (~5 x 10^{-6} moles/ℓ) benzene in cryogenic liquids, there is a much larger temperature dependence of this lifetime for high concentration solutions (2 x 10$^{-5} \leq c \leq$ 2 x 10^{-3} moles/ℓ). Higher concentrations yield, in general, shorter lifetimes. This indicates that

another quenching process begins to operate which must be at least a
bimolecular one. These data also show (Fig. 2-4) that as temperature increases
the relaxation time reaches a minimum value; further increase of the
temperature leads to an increase in the $^1B_{2u}$ fluorescence lifetime. This
anomalous behavior in the cryogenic liquids C_2H_4, C_2H_6, and C_3H_8 is
consistent with the formation of bilmolecular excimers which quench the excited
monomer. At higher temperatures ($\sim150 \leq T \leq 220K$), the dissociation of
excimers repopulates the excited $^1B_{2u}$ of the monomer, thereby leading to
an increase in the observed fluorescence lifetime.

In order to demonstrate that the above process is the correct description
for the observed lifetime behavior, it is necessary to present a kinetic scheme
which, for specific values of the parameters, will generate such complex be-
havior with temperature and solute concentration. The discussion below follows
closely the discussion of Birks.[12] Fig. 6 shows the rate processes considered
for the monomer/excimer systems and gives an explanation of the notation. For
pulsed excitation, the rate equations governing the excited state monomer and
excimer are

$$\frac{d[M^*]}{dt} = -(k_{FM} + k_{IM} + k_{DM}[M]) [M^*] + k_{MD} [D^*] \tag{1}$$

$$\frac{d[D^*]}{dt} = k_{DM} [M][M^*] - (k_{FD} + k_{ID} + k_{MD}) [D^*] \tag{2}$$

in which:

[M] is the concentration (moles/ℓ) of ground state benzene;

[M*] is the concentration (moles/ℓ) of excited state benzene;

11

$[D^*]$ is the concentration (moles/ℓ) of excited state dimer (excimer) benzene, and k_{FM}, k_{FD}, k_{IM} and k_{ID} are the fluorescence rate (s^{-1}) of the monomer, the fluorescence rate of the excimer, the total nonradiative rate of monomer, and the total nonradiative rate of the excimer, respectively; k_{DM} [M] is the rate of formation of the excimer from the combination of an excited monomer and a ground state monomer; and k_{MD} is the dissociation rate of the excimer to form an excited monomer and a ground state monomer.

Applying the initial conditions that at t = 0, $[M^*] = [M^*]_0$ and $[D^*] = 0$, the solutions of eq. (1) and (2) can be written [12]

$$[M^*] = [M^*]_0 \frac{\lambda_2 - x}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} + A e^{-\lambda_2 t}) \qquad (3)$$

$$[D^*] = [M^*]_0 \frac{k_{DM}[M]}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \qquad (3)$$

in which

$$x = k_M + k_{DM} [M]$$

$$y = k_D + k_{MD}$$

$$k_M = k_{FM} + k_{IM}$$

$$k_D = k_{FD} + k_{ID}$$

$$A = \frac{x - \lambda_1}{\lambda_2 - x}$$

$$\lambda_{1,2} = \frac{x+y}{2} \pm \tfrac{1}{2} [(y-x)^2 + 4 k_{DM} k_{MD}[M]]^{\frac{1}{2}}$$

The temperature dependence of the above rate constants can be written as[10]

$$k_{IM} = k_{IM}{}^0 + k'_{IM}\, e^{\frac{-\Delta E_{M1}}{k_B T}} + k''_{IM}\, e^{\frac{-\Delta E_{M2}}{k_B T}} \tag{5}$$

$$k_{ID} = k_{ID}{}^0 + k'_{ID}\, e^{\frac{-\Delta E_D}{k_B T}} \tag{6}$$

$$k_{DM}[M] = k'_{DM}[M]\, e^{\frac{-\Delta E_1}{k_B T}} \tag{7}$$

$$k_{MD} = k'_{MD}\, e^{\frac{-\Delta E_2}{k_B T}} \tag{8}$$

k_{FM} and k_{FD} are temperature independent. In the above equations, k_{IM} is the nonradiative rate of the $^1B_{2u}$ excited monomer, $k_{IM}{}^0$ is the temperature independent portion of k_{IM}, and k'_{IM} is the frequency factor of the temperature dependence part of k_{IM} at low temperature. The second term in eq. (5) is about 10% of the total relaxation rate k_M over the range 90–220K for 0.3 ppm (5×10^{-6} moles/ℓ) solutions. The third term on the right of eq. (5) is the rate of the nonradiative pathway that apparently appears at ~2500 cm^{-1} above the zero point level of the $^1B_{2u}$ state. In the temperature range of interest, this term can be ignored. k_{ID} is the nonradiative rate of the excimer and includes two terms: one temperature dependent and one temperature independent. k_{DM} presents a diffusion process with an activation energy $\Delta E_1 = \Delta E_n$, the diffusive activation energy of the solvent. Finally, k_{MD} is the rate of breakup of the excimer which is also a thermally activated rate with activation energy ΔE_2. It is clear from the above discussion that the second term in eq. (5) is small (ΔE_{M1} is small) and plays only a minor role in the overall decay rate for the $^1B_{2u}$ monomer excited state.

Excimer fluorescence is not observed in any of the solutions, most likely due to its width,[10] and therefore, k_{ID} and k_D need to be evaluated from

other parameters. The rate of formation of excimers, $k_{DM}[M]$, is a diffusion controlled process[10,12] and the activation energy for excimer formation ΔE_1 is equal to the activation energy for diffusion processes in the liquid calculated from viscosity data.[13] Computer fitting of the rate data yields, for C_2H_6, C_2H_4, and C_3H_8, an activation energy of ~440 cm^{-1}. The diffusion rate constant, calculated from $k_\eta = \dfrac{8RT}{3000\eta}$ (ℓ/mol sec) with η in poise is approximately k_{DM}. The binding energy B of the excimer in cyclohexane, shown by Birks[10] et al. to be ~5075 cal/mol, can be used to calculate ΔE_2 from $\Delta E_2 = \Delta E_1 + B$.

The other rate constants can be approximately evaluated following the procedures of ref. 10. We define a "half value concentration" C_h at which the quantum yield of the monomer has dropped to half its infinite dilution value, $\phi_M = \frac{1}{2}\phi_{M_o}$. Since $\phi_{M_o} = k_{FM}\tau_o$ and $\phi_M = k_{FM}\tau$ evaluating the lifetime at different concentrations would result in information concerning C_h. Then,[10]

$$C_h = \frac{k_M(k_D + k_{MD})}{k_D k_{DM}} \quad . \tag{9}$$

At high temperature, for which $k_{MD} \gg k_D$, one obtains the relation

$$k_D \sim k_M \; \frac{1}{C_h} \; \frac{k_{MD}}{k_{DM}} \quad . \tag{10}$$

The relationship between k_{MD} and k_{DM} can be evaluated from the thermodynamic relations for the monomer/excimer system at equilibrium using

$$\Delta G = -RT \ln \left(\frac{k_{DM}}{k_{MD}}\right) = \Delta H - T\Delta S \tag{11}$$

in which ΔG, ΔH, ΔS, R, T have their usual meanings and standard states.[10]
S is probably not temperature dependent but could vary slightly from solvent to
solvent. Assuming $H = \Delta E_1 - \Delta E_2 = -B$, and adopting the values for benzene in
cyclohexane ($\Delta H \sim -5075$ cal/mole and $\Delta S \sim -20.3$ cal/mole K) one obtains the
values of k_{DM}/k_{MD} at different temperatures.

Using this overall scheme and the roughly evaluated rate constants described
above, it is possible to rationalize the overall anomalous behavior for
fluorescence of benzene in low temperature liquids. It should be kept in mind
that this discussion does not represent a proof of the scheme but shows that
the experimental results can be fitted within the scope of the kinetic model.
All rate constants could not be evaluated from λ_1 and λ_2 because only single
exponential decays are observed and no excimer fluorescence was found. More
will be said about this at the end of this section.

In the low temperature range ($T \leq 120K$), for which $k_M \gg k_{DM}[M]$ and
$k_D \gg k_{MD}$ can be assumed, expressions for λ_1 and λ_2 can be approximated to

$$\lambda_1 \sim x$$

$$\lambda_2 \sim y$$

and $A = \dfrac{x-\lambda_1}{\lambda_2-x}$ approaches 0. Under these conditions, the effective decay rate of
the excited monomer can be described as a single exponential decreasing function.
This rate is $k \sim k_M + k_{DM}[M]$. At low concentrations, for which bimolecular
reactions can be neglected, the decay rate $k \sim k_M$. The results show that k_M
is only slightly temperature dependent (Fig. 2-4). Increase of the solute
concentration makes the bimolecular quenching more important. The difference
between the decay rates of two different concentration solutions indicates a

16 Blank

process with an associated activation energy approximately equal to the activation energy for the diffusion process calculated from solvent viscosity data. Thus, k_{DM} is roughly equal to the diffusion rate constant, excimer formation is diffusion controlled, and the probability of excimer formation from the collision of an excited and ground state monomer is close to unity. This efficient formation of the excimer can be realized in terms of a solvent cage trapping of the pair of molecules. At low temperature, once such a solvent structure traps the excited and ground state molecules, reseparation is difficult due to the surrounding solvent shell potential well.

At higher temperature (T ~ 150K), for which the reverse conditions exist ($k_{DM}[M] > k_M$ and $k_{MD} > k_D$), the effective rate parameters are

$$\lambda_1 \sim \frac{k_M k_{MD} + k_D k_{DM}[M]}{k_{MD} + k_{DM}[M]} \tag{12}$$

$$\lambda_2 \sim k_{MD} + k_{DM} M + \frac{k_D k_{MD} + k_M k_{DM}[M]}{k_{MD} + k_{DM}[M]} \tag{13}$$

and

$$A = \frac{1 + \dfrac{k_{DM}[M]}{k_{MD}} + \dfrac{k_M - k_D}{k_{MD}}}{1 + \dfrac{k_{MD}}{k_{DM}[M]} - \dfrac{k_M - k_D}{k_{MD}}} \ .$$

It is clear that $\lambda_2 \gg \lambda_1$ and A is only about unity. As one can see from Table I, the components of the second term in eq. (3) will decay in a few ns. Thus, λ_1 is the same order of magnitude as k_M and this will be the

observed effective decay rate based on the experimental time resolution.

Physically this condition implies that the monomer and excimer are in dynamic

equilibrium; λ_1 is then the rate at which electronic excitation is lost from

the system with $[M^*]$ and $[D^*]$ in equilibrium.

All the above rate constants are temperature dependent as discussed in

eq. (5-8). However, the intrinsic temperature depednence of k_M is weak and

we can assume the same is true for k_D; to a first approximation we will

neglect the two temperature dependent components of k_M and k_D. In order to

determine the residual temperature behavior of λ_1, the temperature deviation

of λ_1 can be obtained approximately as

$$\frac{d\lambda_1}{dT} = \frac{k_{MD}k_{DM}[M](k_M-k_D)(\Delta E_2-\Delta E_1)/k_B T^2}{(k_{MD} + k_{DM}[M])^2} \quad .$$

Since every term in this expression is positive and $\Delta E_2 > \Delta E_1$, the fact that

$k_D > k_M$ in the high temperature range makes it clear that $\frac{d\lambda_1}{dT} < 0$ (see Table

I). Therefore, further increase in the temperature in this temperature domain

will reduce the relaxation rate (increase the relaxation time) as is observed.

The relation $k_D > k_M$ in this temperature range is also verified from the

concentration derivative of λ_1 (in eq. (12)) for which experimental results

give $\frac{d\lambda_1}{d[M]} > 0$ under the above conditions.

These arguments would in principle apply to even higher temperatures

(room temperature liquids for example), but the third term on the right hand

side of eq.(5) eventually becomes dominant. Thus, the thermally activated

process to the effective quenching channel ~2500 cm^{-1} above the zero point

level of $^1B_{2u}$ takes place at these elevated temperatures and eventually re-

duces the lifetime of the excited state. Again, this is in accord with the

usual observations.

Although the possibility of the increasing lifetime of singlet benzene in small molecular liquids due to triplet-triplet annihilation cannot be completely ruled out from our experimental results, three other observations indicate it is unlikely:

a) the fluorescence intensity is linear with input power over all powers and concentrations employed (less than 0.1 to 3 mJ/pulse) and ($\sim 2 \times 10^{-6}$ to $\sim 2 \times 10^{-3}$ moles/ℓ);

b) pyrazine triplet lifetime is 4 ms in c_2H_6 and C_3H_8 at 90K and 50 μs at 150K;[14] and

c) naphthalene has been reported to have a 0.5 s triplet lifetime near room temperature in the liquid state.[15]

It is, therefore, rather unlikely that the singlet state can be repopulated via the triplet state to yield the increased lifetimes observed here above ca. 150K. A somewhat more definitive experiment, adding $\sim 6 \times 10^{-4}$ moles/ℓ O_2 to these solution, shows an increase in fluorescence lifetime at high temperatures just as solutions without O_2. This further demonstrates that the monomer/excimer model is a reasonable approach to the description of the micro-kinetics of excited benzene in cryogenic liquid solutions for the duration of the fluorescence (~ 100 ns). The various rates shown in Table I indicate that the low temperature and high temperature limits are acceptable assumptions.

Finally, consider the results, presented in Fig. 5, for the $^1B_{2u}$ fluorescence lifetimes in C_3H_6 and $1-C_4H_8$ as a function of temperature and concentration. Since these lifetimes are independent of concentration, the possibility of self-quenching can be ruled out as a dominant process. The

temperature dependence of the lifetime in these solvents follows a thermal activation process with an activation energy close to the activation energy for diffusion. Two possible causes for such behavior can be considered: impurity quenching and intrinsic solvent triplet state quenching of the $^1B_{2u}$ state.

For impurity quenching, the concentration of impurities would have to be 100 ppm for a unit probability of quenching upon diffusional encounters. An impurity concentration this high after numerous serial purification procedures seems quite unlikely. Moreover, two different solvents, C_3H_6 and $1\text{-}C_4H_8$, are involved, both of which yield the same concentration and temperature dependences for the $^1B_{2u}$ state. The experimental results for benzene and naphthalene[14] (for which these are not unique solvents) further indicate that the quenching impurities in these systems must have singlet energy levels between the $^1B_{2u}$ state of benzene and the $^1B_{3u}$ state of naphthalene. Such impurities could account for the quenching of the benzene but not the naphthalene lifetime. Under these circumstances ketones and aldehydes of solvent-like molecules might represent reasonable candidates for the quenchers. However, the purification procedures discussed in the Experimental Section should reduce the concentration of such species considerably in repeated steps; probably below 100 ppm. Similar experiments with pyrazine[14] reveal that $^3B_{3u}$ phosphorescence is quenched in C_2H_4, as well as in C_3H_6 and $1\text{-}C_4H_8$ solvents, making it unlikely that impurities play a significant role in the overall excited state kinetics, in general.

A rather more likely possibility is that the solvents themselves are responsible for the new $^1B_{2u}$ quenching mechanism in benzene/C_3H_6 and $1\text{-}C_4H_8$ solutions. From electron impact experiments[16] it has been shown

that C_2H_4, C_3H_6 and $1-C_4H_8$ all have a triplet state at ca. 34000^{-1}.

The latter two triplet states could act as effective quenchers of the $^1B_{2u}$

state with a quenching probablity of roughly 2×10^{-3} per collision based on

Fig. 5 and viscosity data. Such a low quenching probability would be expected

for singlet-triplet energy transfer. The much lower probability (see Figs.

2-4) for $C_2H_4/^1B_{2u}$ quenching may be related to slight energy differences

or size/geometry affects on the details of the collision process itself. On

the other hand, the naphthalene $^1B_{3u}$ could not be trapped based on energy

considerations and the pyrazine $^3B_{3u}$ could be trapped in the intersystem

crossing process involving higher triplet states. Thus, while the question is

certainly not settled, we do favor an intrinsic triplet state solvent quenching

mechanism for the $^1B_{2u}$ state of benzene in C_3H_6 and $1-C_4H_8$ solvents.

Since the kinetics model for these results predicts a number of pathways

are involved in the relaxation process, one would expect non-exponential, or

at least multiexponential, experimental decays to arise. As indicated above,

such behavior is not observed. Computer simulation of a single decay curve

composed of two exponential components reveals that the observed total decay

will be dominated by the major intensity contributor if both exponentials

have the same orders of magnitude decay constant. On the other hand, if the

decay rates are of different order of magnitude, the observed lifetime will

be dominated by the component with the longer decay constant assuming they

both contribute with the same intensity factor. The estimated rate constants

presented in Table I indicate that at high t-mperature the observed lifetime

will be mainly due to the monomer decay rate; at low temperatures the observed

decay constant will also be determined by the monomer rate constant due to the

low excimer population. At intermediate temperatures (including the turning

point) the population of the excimer is smaller than the monomer and thus one

still observes an apparent single exponential decay constant. Clearly,

higher signal to noise ratio, especially at long times, should reveal multi-

exponential behavior. Thus, this model seems to be capable of addressing the

experimental observations qualitatively; a quantitative theoretical fit proves

not useful here because too many adjustable parameters are available in the

rate equations and too few experimental component rate constants are observable.

V.   SUMMARY AND CONCLUSIONS

The fluorescence lifetime of the $^1B_{2u}$ state of benzene has been investigated in cryogenic solvents. The observed anomalous temperature dependence of this lifetime in C_2H_4, C_2H_6 and C_3H_8 solvents is attributed to the formation at low temperature and dissociation at higher temperature of benzene excimers. The effective cage structure of the local environment within the solvent provides for isolation of the excited monomers but as diffusion brings local cages together with two monomers (one in the $^1A_{1g}$ and the other in the $^1B_{2u}$), an excimer is trapped and maintained within the cage. At higher temperatures, the thermal kinetic energy overcomes this cage-like environment resulting in the dissociation of excimers to generate $^1B_{2u}$ and $^1A_{1g}$ monomers. The fluorescence lifetime in low concentration samples of the above solvents at low temperature is within experimental error of that of the isolated molecule in the gas phase; this lifetime varies little over the entire temperature range of these liquids. The implication here is that the small thermal kinetic energy available at low temperature (80–220K) does not quench the $^1B_{2u}$ state of benzene even though the collision frequency is extremely high. Caging effects of the solvent, that is some structural stability of the solute-solvent shell system, are consistent with such evidence. The observation of a high rate of relaxation for benzene in room temperature liquids is most likely due to a thermal nonradiative quenching pathway ~2500 cm^{-1} above the zero point level of the $^1B_{2u}$ state.

The different $^1B_{2u}$ lifetime behavior found for the C_3H_6 and $1-C_4H_8$ solvent systems is tentatively attributed to $^1B_{2u}$/triplet state solvent

collisional energy transfer. The possibility of impurity quenching for these solvents is argued to be less likely.

24

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26

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TABLE I

Estimates of the rate constants for C_6D_6 fluorescence in C_2H_6 solvent as a function of temperature. See text and Fig. 6 for details concerning the processes and the overall scheme.

T(k)	(1) C_h(mole/ℓ)	(2) $\frac{k_{DM}}{k_{MD}}$ (ℓ/mole)	k_M(s^{-1})	(3) $k_{DM}[M]$(s^{-1})	(4) k_D(s^{-1})	k_{MD}(s^{-1})
90	7.6×10^{-3}	8.1×10^{7}	$\sim6\times10^{6}$	4.0×10^{5}	$\sim2\times10^{6}$ (5)	1.0×10^{1}
120	1.7×10^{-3}	6.6×10^{6}	$\sim6\times10^{6}$	2.3×10^{6}	$\sim2\times10^{6}$ (5)	6.0×10^{4}
150	9.5×10^{-4}	9.2×10^{2}	$\sim6\times10^{6}$	6.3×10^{6}	6.8×10^{6}	1.2×10^{7}
160	5.7×10^{-4}	3.2×10^{2}	$\sim6\times10^{6}$	8.0×10^{6}	3.3×10^{7}	4.4×10^{7}
170	1.1×10^{-3}	1.2×10^{2}	$\sim6\times10^{6}$	1.0×10^{7}	4.5×10^{7}	1.5×10^{8}
180	1.9×10^{-3}	5.3×10^{1}	$\sim6\times10^{6}$	1.3×10^{7}	6.0×10^{7}	4.3×10^{8}

(1) evaluated from concentration dependence of the fluorescence lifetime at each temperature

(2) calucated from $e^{\frac{1}{R}(-\frac{\Delta H}{T} + \Delta S)}$. Values of ΔH and ΔS taken from ref. 10.

(3) assumes 30 ppm (5.7×10^{-4} moles/ℓ) of C_6D_6 in C_2H_6 and viscosity data of C_2H_6

(4) calculated from $k_D = k_M \frac{1}{C_h} \frac{k_{MD}}{k_{DM}}$ at high temperature

(5) estimated order of magnitude

FIGURE CAPTIONS

Figure 1

Fluorescence intensity as a function of time for 4 ppm C_6D_6 in liquid C_2H_6 at 90K, 150K and 180K. The lines through the data are computer least squares fits to the decay function with relaxation times as indicated in the figure.

Figure 2

Temperature dependence of the fluorescence lifetime of C_6D_6 in C_2H_6 ((X) 0.3 ppm, ($\wedge$) 8 ppm, and (0) 56 ppm). (at 90K 1 ppm $\sim 1.9 \times 10^{-5}$ moles/ℓ)

Figure 3

Temperature dependence of the fluorescence lifetime of C_6D_6 in C_3H_8 ((X) 0.3 ppm, (Δ) 18 ppm and (0) 90 ppm). (at 90K 1 ppm $\sim 1.3 \times 10^{-5}$ moles/ℓ)

Figure 4

Temperature dependence of the fluorescence lifetime of C_6D_6 in C_2H_4 ((X) 0.3 ppm, (Δ) 8 ppm and (0) 32 ppm). (at 90K 1 ppm $\sim 2 \times 10^{-5}$ moles/ℓ)

Figure 5

Temperature dependence of the fluorescence lifetime of C_6D_6 in C_3H_6 and $1-C_4H_8$ ((X) 0.3 ppm in C_3H_6, ($\square$) 2 ppm in C_3H_6, (0) 91 ppm in C_3H_6, (+) 0.3 ppm in $1-C_4H_8$, (Δ) 8.3 ppm in $1-C_4H_8$). (at 90K 1 ppm in $1-C_4H_8$ is $\sim 1.3 \times 10^{-5}$ moles/ℓ and in C_3H_6 is $\sim 1.4 \times 10^{-5}$ moles/ℓ)

Figure 6

Rate processes for monomer/excimer formation and decay.

k_{FM} is the radiative rate for the excited monomer.

k_{IM} is the nonradiative rate for the excited monomer.

k_{FD} is the radiative rate for the excimer.

k_{ID} is the nonradiative rate for the excimer.

$k_{DM}[M]$ is the formation rate of the excimer from an excited monomer and a ground state monomer.

$[M^*]$ is the concentration of the excited monomer (moles/ℓ).

$[D^*]$ is the concentration of the excimer (moles/ℓ).

$[M]$ is the concentration of the solute ground state (moles/ℓ).

Formation of the excimer is a diffusion controlled process with an activation energy equal to the activation energy for diffusion processes in the solvent ($\Delta E_n = \Delta E_1 = E_{DM} - E_M$). The dissociation of an excimer to form an excited state monomer and ground state monomer breaks the excimer bond ($B = \Delta E_2 - \Delta E_1 = E_M - E_D$). The activation energy ΔE_2 ($\Delta E_2 \gg \Delta E_1$) is associated with this dissociation process. The fluorescence peak of the monomer appears at $[E_M - E_{M_o}]$ and the fluorescence peak of the excimer appears at $E_D - E_{D_o}$.

C_6D_6 / C_2H_6

$T_1 = 154\,ns$

90K

$T_1 = 116\,ns$

150K

$T_1 = 137\,ns$

180K

INTENSITY (ARBITRARY UNIT)

TIME (ns)